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Kinetics and Mechanism of the Chlormethyloxirane Reaction with Phenols Catalyzed by Tertiary Amines and Pyridine Derivatives

E. N. Shved, E. N. Petrenko, and M. A. Pozhidaev

Donetsk National University, Donetsk, 83055 Ukraine

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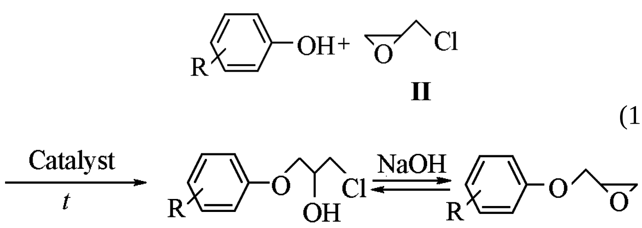
Reaction of phenols with 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) proceeds along a scheme [1]:



(1)

Although a great number of patents demonstrates the practical importance of reaction (1) its catalysis, kinetics, and selectivity is poorly understood [1–3]. The most important for investigation is the first reaction stage, formation of chlorohydrin ether, since just this stage is rate-limiting [4]. Some published data indicate that the first stage of reaction (1) is first order with respect to each reagent [5]. However our preceding studies [6] showed that the calculation of the apparent rate constant by the law of the overall second order was not always satisfactory: in some cases the rate constants monotonically increased. It was established [1, 6] that amines and ammonium salts in reaction (1) play the role of basic catalysts. Therefore the catalysis mechanism in phenols reaction with compound **II** may be represented by a scheme [7]:

$$\mathrm{A + M} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{AM}, \quad \mathrm{AM + B} \overset{k_2}{\rightleftarrows} \mathrm{AB + M}$$

where A is phenol, B is epichlorohydrin, M is catalyst.

In the framework of quasi-stationary approximation using the material balance with respect to phenol and catalyst three cases are presumable:

$$(1)\quad k_1[\mathrm{A}] >> k_{-1} + k_2[\mathrm{B}]_0, \quad -\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{B}]_0[\mathrm{M}]_0; \qquad (2)$$

$$(2)\quad k_1[\mathrm{A}] << k_{-1} + k_2[\mathrm{B}]_0, \quad -\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2[\mathrm{B}]_0}{k_{-1} + k_2[\mathrm{B}]_0}[\mathrm{A}][\mathrm{M}]_0; \qquad (3)$$

$$(3)\quad k_1[\mathrm{A}] \approx k_{-1} + k_2[\mathrm{B}]_0, \quad -\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2[\mathrm{B}]_0[\mathrm{A}][\mathrm{M}]_0}{k_{-1}[\mathrm{A}] + k_{-1} + k_2[\mathrm{B}]_0}. \qquad (4)$$

In the majority of the studied cases of reactions belonging to type (1) according to literature data [4, 6] operates the second case (3).

It was important to find out the possibility of realization for the first case (2) in order to support our assumptions. To increase the equilibrium constant ($K_c = k_1/k_{-1}$) we selected phenols with low pK_a values [3-chlorophenol (**Ia**) and 4-nitrophenol (**Ib**)]. As catalysts are applied pyridine derivatives (2,5-dimethylpyridine, 2,4,6-trimethylpyridine, *N*-methylpyridinium iodide) that are characterized by high polarizability [7], and also tributylamine.

From the experimental kinetic curves of phenol **Ia, b** consumption was graphically estimated the zero order of reaction in phenol concentration (Fig. 1). A set of straight lines was obtained in coordinates ($a - x$) vs t with correlation factors $r > 0.98$ and phenol conversion on the average up to 80%. Taking into account the pseudo-first order of the reaction in epoxy compound **II** the apparent rate constants (k_{app}) were calculated by the following equation with the use of the least-squares method:

$$k_{app} = x/tb, \qquad (5)$$

where x is the quantity of the reacted phenol **Ia, b**, mol l^{-1}, b is the concentration of compound **II**, mol l^{-1}, t is reaction time, s. From the relation of k_{app} to the catalyst concentration (m, mol l^{-1}) (Fig. 2) was established the first order of reaction in catalyst and were calculated the rate constants for catalytic (k_c) and noncatalytic (k_0) reaction flows:

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$$k_{app} = k_0 + k_c m. \qquad (6)$$

With catalyst of such high basicity as tributylamine and methyl-substituted pyridine derivatives reaction (1) is of zero order with respect to phenol. It is interesting that *N*-methylpyridinium iodide having iodide ion I^- as an active site is intermediate in catalytic activity between the aliphatic amine (tributylamine) and heteroaromatic amines (di- and trimethylpyridines) which may be related to its high basic properties. The data in table permit the conclusion that the first kinetic case (2) is observed when the rate of complex formation between the phenol and the catalyst is higher than the rate of phenol consumption at the start of the reaction. This is apparently due to formation of associate through a hydrogen bond or of an ion pair from phenol and the catalyst [7]. The zero order in 4-nitrophenol for the uncatalyzed reaction is most likely related to formation of a phenoxide anion because of high acidity of phenol **Ib**.

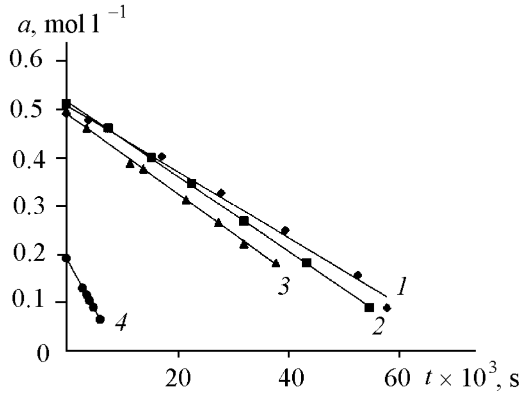


Fig. 1. Phenol consumption as a function of time in reaction with epoxy compound **II** at 80°C: (*1*) 4-nitrophenol (**Ib**), (*a*) 0.498, catalyst 2,6-dimethylpyridine; (*2*) 4-nitrophenol (**Ib**), (*a*) 0.525, catalyst 2,4,6-trimethylpyridine; *3*, 4-nitrophenol (**Ib**), (*a*) 0.505, catalyst *N*-methylpyridinium iodide; (*4*) 3-chlorophenol (**Ia**), (*a*) 0.192, catalyst tributylamine.

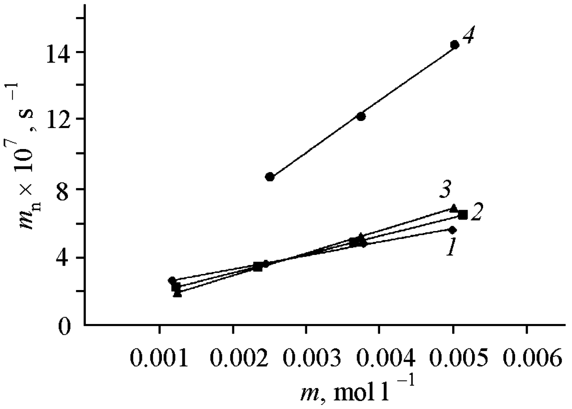
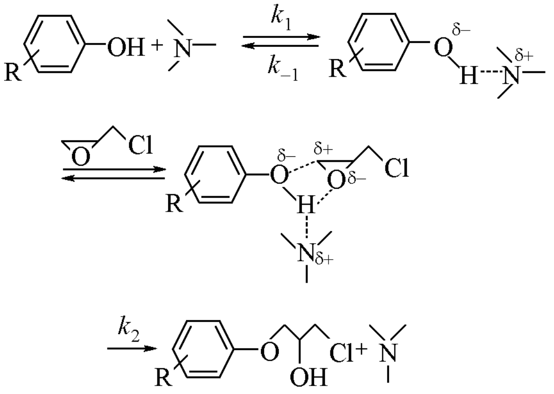


Fig. 2. Dependence of the apparent rate constants of reaction (1) at 80°C on catalyst concentration: (*1*) 4-nitrophenol (**Ib**), catalyst 2,6-dimethylpyridine; (*2*) 4-nitrophenol (**Ib**) catalyst 2,4,6-trimethylpyridine; *3*, 4-nitrophenol (**Ib**), catalyst *N*-methylpyridinium iodide; (*4*) 3-chlorophenol (**Ia**), catalyst tributylamine.

Thus within the framework of the general mechanism of basic catalysis assuming primary interaction of phenol with catalyst we can suggest the following path of the first stage in reaction (1):



Catalysis with *N*-methylpyridinium iodide occurs analogously but instead of the nitrogen the part of the nucleophilic site plays the iodide anion; the reaction order with respect to phenol depends on the ratio of the rate constants of individual reaction stages that in their turn are related to acidic and basic characteristics of the phenol and the catalyst.

Compound **II** was dried on solid sodium hydroxide and then it was distilled at the atmospheric pressure, bp 116.5°C [8]. Compound **Ia** and amine catalysts were distilled at reduced pressure. The corresponding boiling points are as follows: compound **Ia**, 214°C [8]; 2,6-dimethylpyridine, 144°C [8], 2,4,6-trimethylpyridine, 170.4°C [8], tributylamine, 213°C [8].

Compound **Ib** was twice recrystallized from benzene with filtering the hot solution through a layer of alumina, mp 113°C [8].

N-Methylpyridinium iodide was recrystallized from a mixture ethanol–ethyl ether, dried in desiccator over P_2O_5, mp 123–125°C [8].

Procedure for kinetic measurements. The catalyst and the phenol were dissolved in compound **II** (in 1 and 2 ml respectively). The solutions obtained were

Rate constants k_{app} and k_c of reaction between epichlorohydrin (**II**) (b 12.4 mol l^{-1}) and phenols **Ia, b** at 80°C in the presence of different catalysts

Phenol no.	a, mol l^{-1}	Catalyst	m, mol l^{-1}	$k_{app} \times b \times 10^7$, s^{-1}	$k_c \times 10^4$, l mol^{-1} s^{-1}
Ib, pK_a 7.15 [8]	0.747	–	–	0.990±0.024[a]	–
	0.390			0.940±0.010	
Ib	0.498	2,6-Dimethylpyridine, pK_a 6.62 [8]	0.00498	6.02±0.27	9.03±0.13
			0.00378	4.87±0.08	
			0.00245	3.72±0.09	
			0.00119	2.58±0.03	
Ib	0.524	2,4,6-Trimethylpyridine, pK_a 7.43 [8]	0.00512	6.66±0.06	11.1±0.3
			0.00365	5.17±0.01	
			0.00234	3.55±0.05	
			0.00124	2.42±0.01	
Ib	0.505	*N*-Methylpyridinium iodide	0.00500	7.02±0.14	1.34±0.00
			0.00375	5.37±0.10	
			0.00125	2.01±0.10	
Ia, pK_a 9.02 [8]	0.192	Tributylamine, pK_a 10.89 [8]	0.00500	1.64±0.01	3.10±0.16
			0.00375	1.22±0.04	
			0.00250	0.87±0.04	

[a] The given rate constants correspond to uncatalyzed reaction.

kept in a thermostat at 80±0.1°C for 10 min, then the solutions were mixed, and this moment was considered as the initial moment of reaction. After a definite time interval the reaction was stopped by quenching with 10 ml of aqueous 2-propanol (1 : 1) and cooling to room temperature. The mixture was quantitatively transferred into the titration cell and diluted with water. The amount of unreacted compound **I** was determined by potentiometric acidimetric titration with 0.2 N NaOH solution.

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